CLS Example

This example shows how to compute Classical Least Squares (CLS) predictions.

Supporting Information

A Practical Guide to Chemometric Analysis of Optical Spectroscopic Data

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CLS Algorithm

The CLS Algorithm is encapsulated in the following MATLAB function.

```
function [C_cls, B_cls, K_cls] = pnnl_cls(A_train, C_train, A_unknown)
    %pnnl_cls Classical least squares (CLS) regression
    %
    %   [C_cls, B_cls, K_cls] = pnnl_cls(A_train, C_train, A_unknown)
    %   returns concentration matrix C_cls, the least-squares solution that
    %   minimizes norm(C_cls*K_cls - A_unknown), of the Beer's law
    %   relationship CK=A.  Extinction coefficient matrix K_cls is the
    %   least-squares solution that minimizes norm(C_train*K - A_train)
    %   where A_train is a matrix of training spectra corresponding to
    %   known concentrations in the C_train matrix.  Multiplier matrix
    %   B_cls is the pseudo-inverse of Beer's law extinction coefficient
    %   matrix K_cls such that C_cls = A_unknown * B_cls.
    %
    %   Example:
    %
    %     load pnnl_napalm_data
    %     [C_cls, B_cls, K_cls] = pnnl_cls(A_train, C_train, A_unknown);
    %
    %   See also pnnl_pcr, pnnl_pls.

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    % Compute K that minimizes norm(CK - A) given C and A
```

```
        K_cls = C_train \ A_train;

        % Compute C that minimizes norm(CK - A) given A and K
        C_cls = A_unknown / K_cls;

        % Multiplier matrix B_cls is the pseudo-inverse of Beer's law
        % extinction coefficient matrix K_cls such that
        % C_cls = A_unknown * B_cls.
        B_cls = pinv(K_cls);

    end
```

Concentration Data

The concentrations of the training data are in matrix `C_train` and the concentrations of the validation data are in matrix `C_validation`. Column 1 corresponds to the concentrations in constituent 1 (benzene). Column 2 corresponds to the concentrations in constituent 2 (polystyrene). Column 3 corresponds to the concentrations in constituent 3 (gasoline).

$$C_{\text{train}} = \begin{array}{cccc} \textit{benzene} & \textit{polystyrene} & \textit{gasoline} & \\ 0 & 0 & 100.0000 & 1 \\ 5.1309 & 0 & 94.8691 & 2 \\ 10.0660 & 0 & 89.9300 & 3 \\ 20.1799 & 0 & 79.8201 & 4 \\ 40.0120 & 0 & 59.9878 & 5 \\ 59.9972 & 0 & 40.0028 & 6 \\ 79.8412 & 0 & 20.1588 & 7 \\ 89.8273 & 0 & 10.1727 & 8 \\ 100.0000 & 0 & 0 & 9 \\ 90.0264 & 9.9736 & 0 & 10 \\ 80.1375 & 19.8625 & 0 & 11 \\ 64.9950 & 35.0005 & 0 & 12 \\ 21.0228 & 45.9197 & 33.0575 & 13 \\ 49.9507 & 5.0599 & 44.9895 & 14 \\ 40.0182 & 20.0385 & 39.9433 & 15 \\ 40.0154 & 10.0036 & 49.9810 & 16 \\ 30.0059 & 10.0282 & 59.9659 & 17 \\ 40.0340 & 39.9670 & 19.9990 & 18 \\ 49.9393 & 3.3748 & 46.6859 & 19 \\ 46.6501 & 13.4658 & 39.8840 & 20 \end{array}$$

$$C_{\text{validation}} = \begin{array}{cccc} \textit{benzene} & \textit{polystyrene} & \textit{gasoline} & \\ 22.1665 & 39.0384 & 38.7951 & 1 \\ 21.6874 & 37.0596 & 41.2530 & 2 \\ 22.1665 & 39.6980 & 38.1355 & 3 \\ 26.9575 & 40.3576 & 32.6849 & 4 \\ 25.9993 & 33.7616 & 40.2391 & 5 \\ 23.1247 & 37.0596 & 39.8157 & 6 \\ 22.6456 & 39.0384 & 38.3160 & 7 \\ 22.6456 & 39.0384 & 38.3160 & 8 \\ 27.4366 & 42.3364 & 30.2270 & 9 \\ 27.4366 & 37.7192 & 34.8442 & 10 \\ 26.4784 & 40.3576 & 33.1640 & 11 \\ 26.9575 & 37.7192 & 35.3233 & 12 \end{array}$$

Clear variables and load the PNNL napalm data.

```
clearvars
load pnnl_napalm_data
```

Compute CLS

Set up the plot title and color.

```
title_string = sprintf('CLS');
nConstituents = size(C_validation,2);
colorOrder = pnnl_colorOrder(nConstituents);
```

Use all the columns of `C_train` to compute CLS. Use all the columns of `C_validation` to compute RMSEP (root mean square error predicted). Use the columns of `C_train` to compute RMSEC (root mean square error calibration) and RMSECV (root mean square error cross validation).

Compute CLS

```
C_predicted = pnnl_cls(A_train,C_train,A_unknown);
C_calibration = pnnl_cls(A_train,C_train,A_train);
C_cross_validation = pnnl_cross_validation(@pnnl_cls,A_train,C_train);
```

Compute RMSE

```
RMSEP = pnnl_rmse(C_validation,C_predicted);
RMSEC = pnnl_rmse(C_train,C_calibration);
RMSECV = pnnl_rmse(C_train,C_cross_validation);
```

Display RMSE

```
pnnl_display_rmse(title_string,ConstituentNames,...
    RMSEC,RMSECV,RMSEP);
```

```
-----------------------------------------------------
      CLS       Benzene    Polystyrene       Gasoline
    RMSEC        4.2721         2.3784         5.6857
   RMSECV        5.1043         3.0807         6.7847
    RMSEP         7.895         2.6988         9.1105
-----------------------------------------------------
```

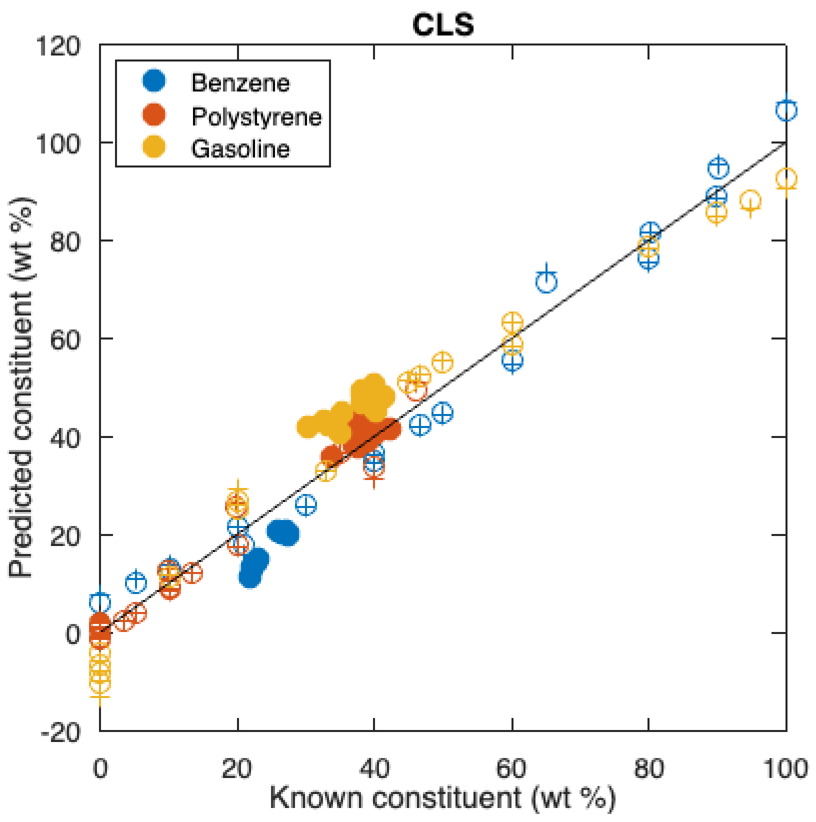
Plot the results

```
figure
h = gobjects(nConstituents,1);
for k = 1:nConstituents
    % Plot Concentrations
    hold on
    % Validation vs. Predicted
    h(k) =
plot(C_validation(:,k),C_predicted(:,k),'.','MarkerSize',35,'Color',colorOrd
er(k,:),'DisplayName',ConstituentNames{k});
    % Train vs. Calibration

plot(C_train(:,k),C_calibration(:,k),'o','MarkerSize',10,'LineWidth',1,'Colo
r',colorOrder(k,:))
```

```
    % Train vs. Crosss Validation

plot(C_train(:,k),C_cross_validation(:,k),'+','MarkerSize',10,'LineWidth',1,
'Color',colorOrder(k,:))
    % 1-1 line
    line(C_train(:,k),C_train(:,k),'Color','k')
    title(title_string)
    xlabel(['Known constituent (',ConcentrationUnits,')'])
    ylabel(['Predicted constituent (',ConcentrationUnits,')'])
    set(gca,'FontSize',14)
    box on
    axis square
    hold off
end
legend(h,'Location','northwest')
```



Legend: Dot is predicted. Circle is calibration. Cross is cross-validation.')

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